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Evaluation of peat and lignite phenanthrene sorption properties in relation to coal petrography: The impact of inertinite

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Abstract

The relationship between phenanthrene sorption properties and petrography of low rank organic particles was investigated to aid in understanding sorption mechanisms, and confirm the previously observed impact of inertinite. Sorption experiments, using phenanthrene as the model organic chemical, were conducted on peat and lignite, of matrix and xylite-rich lithotypes, that have significant differences in inertinite content. Both peat and lignite samples display non-linear isotherms described by the Freundlich model. In general, the sorption isotherm linearity decreases from peat to lignite, and lignite samples show higher sorption capacities ($K_{\mathrm{fr}}=4.2\times10^4$–$4.5\times10^5$) than peat ($K_{\mathrm{fr}}=8.4\times10^3$–$3\times10^4$). Regression analysis applied to the maceral data and sorption parameters showed a strong correlation between inertinite and the variability of isotherm non-linearity. This correlation implies the significant impact of oxidized tissues to the heterogeneity of sorption sites. Moreover, the organic carbon normalized sorption coefficient (K_{oc}), at low phenanthrene concentrations, is related to the inertinite content, as well as to the organic carbon content (on dry, ash-free basis). The degree of inertinite effect on sorption (at low C_e) is higher in lignites than in peat or better, that it increases for samples with increasing organic carbon content (on dry, ash-free basis). This probably suggests that the inertinite content could be a measure of sorption non-linearity and affinity only among samples that have undergone common humification and/or coalification pathways.

Keywords: Inertinite; Maceral analysis; K_{oc}; Phenanthrene sorption; Sorption non-linearity

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1. Introduction

During the last decade there has been widespread discussion on the environmental application of organic petrography (e.g. ICCP, 1994; Ligouis et al., 2005). Significant research has been undertaken on the behaviour of anthropogenic pollutants, and the processes that control it in natural systems, in order to predict the interaction between contaminants and the physical environment (e.g. Chiou, 2002). Sorption is one of the crucial processes that affect the environmental fate and transport of the hydrophobic organic contaminants (HOCs) in earth's subsurface (e.g. Grathwohl, 1990; Xia and Ball, 1999; Karapanagioti et al., 2000; Allen-King et al., 2002 and the references cited therein; Cornelissen and Gustafsson, 2004). It can occur a) as a

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linear absorption process where the contaminant partitions within the organic phase or b) as non-linear processes including accumulation on the organic matter surface (adsorption), filling and condensation within micropores, etc. Although the exact mechanism of sorption process still remains uncertain, the currently most accepted model involves a dual-mode sorption concept (Xing and Pignatello, 1997). According to this concept the organic matter (OM) is distinguished into two main domains displaying different sorption mechanisms: 1. The “soft” organic matter, which corresponds to amorphous lipophilic, gel-like natural organic matrix (e.g. humic and fulvic substances), displaying a linear absorption process, and 2. The “hard” organic matter, which corresponds to the condensed or the oxidized organic matter, that shows non-linear adsorption processes (Luthy et al., 1997; Xing and Pignatello, 1997; Cornelissen and Gustafsson, 2004). Moreover, the sorption mechanism depends on HOCs-concentration relative to their solubility; at low relative concentrations, non-linear sorption is observed and surface adsorption and/or pore filling is proposed as the possible sorption mechanism, whereas at high relative concentrations, partitioning is the dominant mechanism (Xia and Ball, 1999; Chiou et al., 2000).

Previous studies on organic contaminant transport and fate have observed a non-linearity of sorption at low concentrations (Kleineidam et al., 1999; Ghosh et al., 2000; Karapanagioti et al., 2000, 2004; Cornelissen et al., 2004) and employed organic petrography methods to correlate organic matter phases and sediment sorption characteristics. Inertinite has been identified as the maceral group most responsible for high sorption capacity and sorption non-linearity (Karapanagioti and Sabatini, 2000; Karapanagioti et al., 2001, 2004). However, most sorption studies were conducted with sedimentary organic matter (e.g. dispersed organic matter in sediments and soils), which is highly heterogeneous and have a low concentration of organic matter. This heterogeneity does not allow further investigation of the effects of inertinite on the sorption characteristics.

In the present study, we conducted sorption experiments on peat and lignite samples that have been previously characterized using organic petrography methods. Phenanthrene is a hydrophobic organic pollutant commonly used in sorption studies as a model organic chemical and is also used in the present work. The aim is to use sorbents with high organic carbon content for elucidating any correspondence of the dual-mode sorption model of sorbent organic matter to the organic petrographic composition (macerals), and initiating an approach to verify the previously mentioned relationship between inertinite content and sorption characteristics.

2. Materials and methods

Four Late-Miocene lignite samples from the Almyros lignite basin in Central Greece, two peat samples from the Philippi peatland (NE Greece) and two peat samples from the Keri mire (Zakynthos Island, W Greece), have been selected for the sorption experiments (Fig. 1, Table 1). Ash yields were determined according to American Society for Testing and Materials (ASTM 1983, 1989) D3174-89 for lignites and D2974-83 for peat. Ultimate analyses (C, H, N, S) were conducted using a Carlo Erba EA1108 C-H-N-S analyzer. The samples were selected for sorption experiments based on their maceral content, i.e. the selected samples should reveal differences on their composition, concerning primarily the inertinite content. Organic petrography and phenanthrene sorption studies were conducted as follows.

2.1. Organic petrography

The samples were examined using standard coal-petrography techniques. The lignite samples were crushed down to ∅<1 mm and were imbued with epoxy resin (Epofix of STRUERS®) in cylindrical mounts. The peat samples were wet-dehydrated before impregnated with resin. The prepared blocks were grinded using a series of grinding papers (nos. 320, 500, 800, 1200 and 2400), then polished using diamond pastes (∅<3 µm and ∅<1 µm) and finally, alumina suspension (∅<0.06 µm). The polished blocks were microscopically examined using a Leica DMRX microscope. The organic particles were identified under both white reflected and blue excitation light and described according to the nomenclature adopted by the International Committee for Coal and Organic Petrology (ICCP) for low-rank coals (ICCP, 1971, 2001; Sýkorová et al., 2004). Maceral analysis has been performed using point counting (500 counts per block).

2.2. Sorption experiment methods

Phenanthrene was diluted to a 1000 mg/L stock solution in methanol. Solutions used in batch studies were prepared in synthetic water (with 44 mg/L $CaCl_2 \cdot 2H_2O$, 14 mg/L $CaSO_4$, and 17 mg/L $NaHCO_3$) and were spiked with the methanol stock solution to result in initial phenanthrene concentrations of 0.75, 0.5,